as

$$\alpha_H/\alpha_{H_2}=0.8283\pm0.0090. \quad (4)$$

Taking the value $\alpha_{H_2}=(5.564\pm0.028)a_0^3$ for the experimental wavelength of $\lambda=5870$ Å, the value of the dynamic polarizability of the ground state of atomic hydrogen is found to be,

$$\alpha_H=(4.61\pm0.07)a_0^3 \quad (5)$$

with the error assignment on a purely statistical basis.

This result is in good agreement with the theoretical value

$$\alpha_H=(4.66\pm0.01)a_0^3 \quad (6)$$

as calculated using time-dependent perturbation theory[11] and evaluated for the experimental wavelength. Podolsky's calculation[7] and that of Dalgarno and Kingston[10] are accomplished by expanding the index of refraction (or polarizability) in inverse powers of the wavelength in such a way that the sums over intermediate states are eliminated. The value and error assignment quoted above was obtained by a direct, but laborious, evaluation of the second-order perturbation theory from the well known expression for the polarizability of an atom in the nth quantum state,

$$\alpha_n(\omega)=\sum_{n'}\frac{f(n',n)e^2/m}{\omega_{n',n}^2-\omega^2}, \quad (7)$$

which includes a sum over a complete set of states and an integration over the continuum states. Here, ω is the applied angular frequency $(2\pi c/\lambda)$, $\omega_{n',n}$ the Bohr frequencies, and $f(n',n)$ the oscillator strengths.

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Correlation Effects in Atomic Structure Using the Random-Phase Approximation*

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A procedure for treating correlations in atomic structure is introduced and applied to the calculation of excitation energies, oscillator strengths, and photoionization cross sections. The method is the extension of the Hartree–Fock theory known as the random-phase approximation, which has already been applied to a number of other many-body problems. In this application to atomic physics results are given for the following atoms in column II of the periodic table: beryllium, magnesium, calcium, and strontium. These atoms all have ^1S ground states, and only excitations to ^1P states are considered. The general conclusion of the study is that the values of the oscillator strengths and photoionization cross sections are changed significantly by the correlations, while the changes in the values of the excitation energies are quite small. Wherever comparison with experiment is possible, the inclusion of these correlations improves the agreement between theory and experiment. Their effects are, however, not as marked as in highly degenerate infinite systems or in nuclei.

I. INTRODUCTION

A MAJOR problem in theoretical atomic physics, as in other many-particle problems, is the role of correlations, particularly for observables other than the total energy. The only correlations included in the usual first approximation, the Hartree-Fock approximation, are those arising from the Pauli exclusion principle. The value of the total energy of an atom obtained in this way is, of course, quite accurate, being good to within one percent in most cases. The errors in other quantities can, however, be very much greater.

In the past, two main approaches have been followed in improving this situation in atomic physics problems. The variational approach, in which the electronic separations are introduced into the wave function, has had good success for two-electron systems, but has not yet proved practical for heavier atoms. The configuration-interaction method, in which linear combinations of Slater determinants are used, has been mainly useful for light atoms. The results show that the wave function improves very slowly as the number of configurations is increased. Little work has been done on the correlation problem for medium and heavy atoms.

In recent years, however, there has been substantial progress in treating correlations in infinite many-particle systems. In addition to developments in perturbation theory, two nonperturbative approaches have been developed and proved useful in several different contexts. These are the Bardeen, Cooper, and Schrieffer theory of superconductivity,[1] and the random-phase

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approximation used in the theory of the electron gas.[2] Valatin and others have formulated these theories as natural generalizations of the Hartree-Fock approximation.[3] In this context it seems natural to apply these new theories to systems with a finite number of degrees of freedom. This has already been done extensively for atomic nuclei.[4–6] The original successes of these techniques for very large systems does not necessarily mean that they are suitable for finite systems, or even that the conditions for their applicability are the same. Instead, it must be expected that their usefulness will depend on the details of the unperturbed level spectrum and interparticle interaction, and that a demonstration of the smallness of other correlations must be made in each case.

In the present work, the random-phase approximation is applied to some problems in atomic structure. Theoretical values of excitation energies, oscillator strengths, and photoionization cross sections are given for beryllium, magnesium, calcium, and strontium. The correlations of the valence electrons cause significant shifts in the values of the oscillator strengths and photoionization cross sections while the values of the excitation energies are changed very little. This indicates that the Hartree-Fock model may be satisfactory for the calculation of energies and, at the same time, be a poor model for the calculation of other observables. The largest shift in the values of the excitation energies was about 5%, and a shift of this magnitude occurred only for the lowest excited level. For the higher levels, the excitation energies were changed a negligible amount by the correlations. In contrast to this, the values of the resonance oscillator strengths were changed by about 30%, and the values of the oscillator strengths to higher levels were changed by factors of 3 to 20 (one case only). The photoionization cross section near threshold was also shifted a large amount by the correlations. The values of the uncorrelated and correlated cross sections typically differ by a factor of about 5.

The detailed comparison of the numerical results with experimental data is neither possible nor appropriate at this stage. It is not possible because many of the oscillator strengths computed here have not been measured, and very few have been measured more than once, so there remains uncertainty in the correct experimental values. The situation is the same for the photoionization cross sections. The comparison with experiment is not appropriate because of the nature of the computations. It will become clear as the theory is developed in the next section that the Hartree-Fock orbitals would be the best choice for the basis set of states. Because of the great numerical complexity of generating such a basis set, the orbitals used for the basis were generated in either a Hartree or Thomas-Fermi central field. The main purpose of the present calculations has, therefore, been to study the effects of the correlations included in the random-phase approximation, rather than to seek close agreement with experiment. On the other hand, the correlations definitely are in the right direction for improving the agreement between theory and experiment.

Another motivation for this analysis was the possible existence of collective states in atoms similar to the plasmons in the dense electron gas and the states in nuclei responsible for the giant dipole resonance. The present work attacks this question with the same kind of formalism used to treat these other states, but modified to take into account the basic properties of atoms expressed in the independent-particle model wave functions and residual coulomb interactions. For the restricted class of atoms studied, there seems to be little evidence of strong collective effects, although this statement depends somewhat on the particular interpretation placed on the numerical results obtained here. The possibility of such collective states was first studied by Wheeler and Fireman with semiclassical and Thomas-Fermi methods.[7] A similar study has recently been reported by Brandt and Lundqvist.[8]

The theory has been formulated in L-S coupling since this is most suitable for the atoms under consideration. The formulation in terms of j-j coupling can, of course, be made in a straightforward manner. Only excited P states are considered, but continuum as well as bound states are included. The structure of the theory is such that this restriction leads to the inclusion of only the dipole part of the electron-electron interaction.

Although when this work was performed, the experimental situation was quite bad, it is showing signs of improvement. A Russian group recently reported accurate oscillator strengths for the resonance as well as for a few other transitions.[9–12] Except for these results, values for higher transitions are virtually nonexistent. Furthermore, there is no theoretical work on these oscillator strengths. Of the existing theoretical work on resonance oscillator strengths, only Trefftz's

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on magnesium[13] and calcium[14] includes correlation effects. The status of theory and experiment on the photoionization cross sections has recently been reviewed by Ditchburn and Öpik.[15] Taking into account the recent measurement for strontium,[16] the cross sections near threshold are now available for magnesium, calcium, and strontium. On the theoretical side, a Hartree-Fock calculation was made by Bates and Massey in 1941.[17] Indeed, accurate results for the Hartree model have not been generally available, although a program for this purpose has been used for many years at the Rand Corporation.[18] Cooper recently published Hartree calculations for rare-gas atoms, and similar results for column II atoms are presented in this paper.[19] Both Cooper's calculations and the present work are based on the Rand program.

The main theoretical structure for this paper is presented in Sec. II. Here the fundamental equations are derived, properties of the model discussed, and expressions for the oscillator strengths and photoionization cross sections presented. These general formulas are reduced to a form suitable for numerical computation in Sec. III, and some details of the numerical analysis are given. The results for the five atoms studied are then summarized in Sec. IV. Section V contains some discussion of these results.

II. THEORY

A. General Discussion of the Random-Phase Approximation

An important step in the theory of the electron gas was Brueckner and Gell-Mann's perturbation calculation of the ground-state correlation energy.[20] To obtain this result, which is exact in the limit of infinite density, these authors summed the contributions from the "ring" diagrams, each of which is infinite for Coulomb interactions and plane-wave electron states. The difficulties of this kind of perturbation calculation were then circumvented with a canonical Hamiltonian formulation due to Sawada and collaborators.[21,22] It has since been realized that these two methods have practically the same physical basis as the classic work of Bohm and Pines,[2] Landau's theory of the Fermi liquid,[23] and the time-dependent Hartree-Fock theory.[3,24]

Sawada's theory has a number of attractive features. First of all, the effect of dynamical correlations on the properties of excited states can be calculated. Second, the canonical formulation can be easily generalized to other kinds of many-particle systems. Both of these features were exploited in the theory of superconductivity,[25,26] nuclear matter,[27] and finite nuclei,[4–6] and it is these features which permit the extension to atomic structure made in this paper.

The Hamiltonian for an N electron atom contains the Coulomb interaction between the charged particles and various magnetic interactions. For light and medium atoms, the gross term separations are determined by the coulomb interactions, and so the appropriate Hamiltonian is

$$H=\sum_{s=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_s^2-\frac{Ze^2}{r_s}\right)+\frac{e^2}{2}\sum_{s,r=1}^{N}\frac{1}{r_{sr}}$$

$$=\sum_{s=1}^{N}T_s+\tfrac{1}{2}\sum_{s,r=1}^{N}v_{sr}. \tag{1}$$

An effective one-particle potential is introduced, whose eigenfunctions are combined into products to form a basis for the N particle system. The single-particle orbitals satisfy the equation

$$(T_s+V_s)|i\rangle=\epsilon_i|i\rangle. \tag{2}$$

The Hamiltonian is now written

$$H=\sum_{s=1}^{N}(T_s+V_s)+\tfrac{1}{2}\sum_{s,r=1}^{N}v_{sr}-\sum_{s=1}^{N}V_s. \tag{3}$$

The last two terms are called the residual interaction, and V_s is usually chosen to minimize the effect of these terms.

Using the basis defined above, the second-quantized form of Eq. (3) is

$$H=\sum_i \epsilon_i c_i^\dagger c_i+\tfrac{1}{2}\sum_{i,j,k,l}\langle ij|v|lk\rangle c_i^\dagger c_j^\dagger c_k c_l$$

$$-\sum_{i,j}\langle i|V|j\rangle c_i^\dagger c_j, \tag{4}$$

where the operators $c_i^\dagger$ and c_i are Fermion creation and annihilation operators. In the absence of the residual interaction, the ground state would have the lowest N

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electron levels occupied. It is assumed here that this is a nondegenerate state which permits the definition of the "Fermi level" as the completely occupied subshell of least binding energy. One-particle states with energies higher than the "Fermi energy" are called "particle states," and are labeled with Latin letters. The particle operators are given by

$$a_i^\dagger = c_i^\dagger, \quad a_i = c_i. \tag{5a}$$

Those states with energies below the Fermi energy are called "hole states" and are labeled with Greek letters. The hole operators are given by

$$b_\alpha = c_\alpha^\dagger, \quad b_\alpha^\dagger = c_\alpha. \tag{5b}$$

The Hamiltonian is now written in terms of these particle and hole operators

$$H = E_c + K + V_S + V' + W. \tag{6a}$$

The term E_c contains no operators and thus contributes a constant to the eigenvalues of H. However, our concern here is only with excitation energies, and therefore E_c can be neglected. The other terms in H are

$$K = \sum_i \epsilon_i a_i^\dagger a_i - \sum_\alpha \epsilon_\alpha b_\alpha^\dagger b_\alpha, \tag{6b}$$

$$V_s = \tfrac{1}{2} \sum_{i,j,\alpha,\beta} \{\langle ij|v|\alpha\beta\rangle [C^\dagger(i\alpha)C^\dagger(j\beta) + C(i\alpha)C(j\beta)] + 2\langle i\beta|v|\alpha j\rangle_{\rm as} C^\dagger(i\alpha)C(j\beta)\}, \tag{6c}$$

$$V' = V_1 + V_2, \tag{7a}$$

$$V_1 = \tfrac{1}{2} \sum_{i,j,k,l} \langle ij|v|kl\rangle a_i^\dagger a_j^\dagger a_l a_k + \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta|v|\gamma\delta\rangle b_\delta^\dagger b_\gamma^\dagger b_\alpha b_\beta, \tag{7b}$$

$$V_2 = \tfrac{1}{2} \sum_{i,j,k,\alpha} \langle ij|v|k\alpha\rangle_{\rm as} [C^\dagger(j\alpha)a_i^\dagger a_k + a_k^\dagger a_i C(j\alpha)] + \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,i} \langle \alpha\beta|v|\gamma i\rangle_{\rm as} [C(i\alpha)b_\gamma^\dagger b_\beta + b_\beta^\dagger b_\gamma C^\dagger(i\alpha)], \tag{7c}$$

$$W = \sum_{i,j} \gamma_{ij} a_i^\dagger a_j - \sum_{\alpha,\beta} \gamma_{\alpha\beta} b_\alpha^\dagger b_\beta + \sum_{i,\beta} \gamma_{i\beta} [C^\dagger(i\beta) + C(i\beta)]. \tag{7d}$$

The following notation has been introduced in the above equations. The operators $C^\dagger(i\alpha)$ and $C(i\alpha)$ create and destroy a particle hole pair. They are given by

$$C^\dagger(i\alpha) \equiv a_i^\dagger b_\alpha^\dagger, \quad C(i\alpha) \equiv b_\alpha a_i. \tag{8}$$

The subscript as after the states in a matrix element indicates the direct minus exchange term, e.g.,

$$\langle ij|v|kl\rangle_{\rm as} \equiv \langle ij|v|kl\rangle - \langle ij|v|lk\rangle. \tag{9}$$

Finally, the symbol γ_{ij} is defined by

$$\gamma_{ij} = \textstyle\sum_\alpha \langle i\alpha|v|j\alpha\rangle_{\rm as} - \langle i|V|j\rangle. \tag{10}$$

Note that the γ_{ij} would vanish if V were the Hartree-Fock potential.

In the treatment of the electron gas in the random-phase approximation, only K the "kinetic energy," and V_S, the particle-hole interaction, in Eq. (6a) are retained, and the Hamiltonian consisting of these two terms is diagonalized with the aid of some further approximations. Actually, the exchange matrix element appearing in the third term of V_S is not included, as it does not contribute to the correlation energy of the high-density electron gas.

The electron cloud in an atom is physically quite different from the infinite electron gas, however, and if our calculation is to be meaningful, the approximations made in finding the eigenvalues and eigenstates of the Hamiltonian must be reasonable for the treatment of atomic structure. In the next subsection the Hamiltonian is approximately diagonalized, and the approximations made along the way are evaluated in the context of this application to atomic structure.

B. The Eigenvalue Equations

Atomic states in Russell-Saunders coupling are designated by the total orbital and spin angular momentum, their projections on an axis, and the energy. In the following we treat only ^1S ground states whose energy is designated by E_0. The basic variable of the theory is an operator which creates an excited state of H when it acts on the ground state. It is designated by $A^\dagger(LM,SM_S,E)$. The eigenstates of H are designated by $|0\rangle$, $|LM,SM_S,E\rangle$, etc. The equation defining $A^\dagger(LM,SM_S,E)$ is

$$[H,A^\dagger(LM,SM_S,E)] = (E-E_0)A^\dagger(LM,SM_S,E). \tag{11}$$

When both sides of Eq. (11) act on $|0\rangle$, we see that $A^\dagger(LM,SM_S,E)$ has the desired property. Taking the conjugate of Eq. (11) and again letting it act on $|0\rangle$, we see that

$$A(LM,SM_S,E)|0\rangle = 0 \tag{12}$$

because E_0 is the lowest eigenvalue of H. This result will be useful in the derivation of the eigenvalue equations.

It will prove convenient to introduce operators which create and destroy pairs of definite orbital and spin angular momentum. These operators are given by

$$C^\dagger(LM,SM_S,\{i\alpha\}) = e^{i\pi/2} \sum_{m_\alpha,\mu_\alpha} (-1)^{m_\alpha+\mu_\alpha} (l_\alpha - m_\alpha l_i m_i | LM) \times (s_\alpha - \mu_\alpha s_i \mu_i | SM_S) C^\dagger(i\alpha), \tag{13}$$

$$C(LM,SM_S,\{i\alpha\}) = e^{-i\pi/2} \sum_{m_\alpha,\mu_\alpha} (-1)^{m_\alpha-\mu_\alpha} (l_\alpha - m_\alpha l_i m_i | LM) \times (s_\alpha - \mu_\alpha s_i \mu_i | SM_S) C(i\alpha).$$

The quantities l_α, m_α, s_α, μ_α are the orbital and spin quantum numbers describing the single-particle states. The phase of the vector coupling coefficients

is taken from Condon and Shortley.[28] The phase factor, $(-1)^{m_\alpha+\mu_\alpha}$ arises because a particle and a hole are being coupled together, not two particles. The notation $\{i\alpha\}$ indicates that the quantity does not depend on the individual orbital and spin projection quantum numbers. Finally, $e^{i\pi/2}$ is inserted to make the entire coefficient real.

For reasons which will become apparent shortly, the eigenvalue equations are derived by considering the relation

$$\langle LM,SM_S,E|\,(E-H)C^\dagger(LM,SM_S,\{i\alpha\})\,|0\rangle=0, \quad (14)$$

which becomes, after a little manipulation,

$$(E-E_0)\langle LM,SM_S,E|C^\dagger(LM,SM_S,\{i\alpha\})\,|0\rangle-\langle LM,SM_S,E|[H,C^\dagger(LM,SM_S,\{i\alpha\})]\,|0\rangle=0. \quad (15)$$

We further reduce Eq. (15) by using Eq. (12)

$$(E-E_0)\langle 0|[A(LM,SM_S,E),C^\dagger(LM,SM_S,\{i\alpha\})]\,|0\rangle-\langle 0|[A(LM,SM_S,E),[H,C^\dagger(LM,SM_S,\{i\alpha\})]]\,|0\rangle=0 \quad (16)$$

with a similar equation involving $C(L-M, S-M_S, \{i\alpha\})$. Thus far, we have proceeded by formal, exact, manipulations. We must now consider the approximations necessary to obtain solutions to Eq. (16).

The first approximation is to specify the form of $A^\dagger(LM,SM_S,E)$ as

$$A^\dagger(LM,SM_S,E)=\sum_{\{i\alpha\}}[g(LM,SM_S,E,\{i\alpha\})C^\dagger(LM,SM_S,\{i\alpha\}) +h(L-M, S-M_S, E, \{i\alpha\})C(L-M, S-M_S, \{i\alpha\})]. \quad (17)$$

The g's and h's are real amplitudes to be determined by the eigenvalue equations. This form of $A^\dagger(LM,SM_S,E)$ implies that the excited states are expressible mainly as linear combinations of single pair states, i.e., states with one electron excited out of the ground-state configuration. The amplitudes designated by $h(LM,SM_S,\{i\alpha\})$ arise because the operator $A^\dagger(LM,SM_S,E)$ acts on the true ground state in which various numbers of pairs may be excited. By choosing this form of $A^\dagger(LM,SM_S,E)$ we also see that

$$\langle 0|C^\dagger(LM,SM_S,\{i\alpha\})\,|0\rangle=\langle 0|C(LM,SM_S,\{i\alpha\})\,|0\rangle=0, \quad (18)$$

since a matrix of transformation exists between the C operators and the A operators. Further, this matrix is nonsingular because the excited states are linearly independent. Thus, it has an inverse and we can write

$$\langle 0|C^\dagger(LM,SM_S,\{i\alpha\})\,|0\rangle =\langle 0|\sum_{L',S',E}[d(L'M,S'M_S,E,\{i\alpha\})A^\dagger(L'M,S'M_S,E) +e(L'M,S'M_S,E,\{i\alpha\})A(L'M,S'M_S,E)]\,|0\rangle=0.$$

If $A^\dagger(LM,SM_S,E)$ contained a term which accounted for two pair excitations, i.e., a term of the form

$$C^\dagger(LM,SM_S,\{i\alpha\})C^\dagger(L'M',S'M_S',\{j\beta\})$$

by the same argument as above, we would find

$$\langle 0|C^\dagger(LM,SM_S,\{i\alpha\})C^\dagger(L'M',S'M_S',\{j\beta\})\,|0\rangle=0, \quad \langle 0|C(LM,SM_S,\{i\alpha\})C(L'M',S'M_S',\{j\beta\})\,|0\rangle=0. \quad (19)$$

We are completely neglecting the two pair excitations, but we still assume that Eqs. (19) hold.

It should be noted that cases exist for which Eq. (17) is not a suitable approximation. For example, calcium and strontium have low-lying levels which are best described as having both valence electrons excited. Such levels are not accounted for by our choice of the form of $A^\dagger(LM,SM_S,E)$ and their existence has an adverse effect on the numerical results for these two atoms as will be seen in Sec. IV.

Since the form of $A^\dagger(LM,SM_S,E)$ has been prescribed, the commutators in Eq. (16) can be evaluated. All operators in Eq. (16) are products of Fermion creation and annihilation operators so it is straightforward to evaluate their commutators. For example,

$$[C(i\alpha),C(j\beta)]=[C^\dagger(i\alpha),C^\dagger(j\beta)]=0,$$
$$[C(i\alpha),C^\dagger(j\beta)]=\delta_{ij}\delta_{\alpha\beta}-\delta_{\alpha\beta}a_j^\dagger a_i-\delta_{ij}b_\beta^\dagger b_\alpha.$$

The next approximation is now made. It consists of assuming that the ground-state configuration is a good approximation to the true ground state. To put it more precisely, consider an expansion of the true ground state

$$|0\rangle=\xi_0|\Phi_0\rangle+\textstyle\sum_s\xi_s|\Phi_s\rangle, \quad (20a)$$

where $|\Phi_0\rangle$ is the ground-state configuration and the $|\Phi_s\rangle$ are any excited configurations. The assumption made here is that

$$\xi_0\approx 1, \quad \xi_s\ll 1. \quad (20b)$$

Thus, we will ignore any quantity that contains products of the ξ_s's, but retain those quantities that contain first powers of the ξ_s. For example, $\langle 0|a_i^\dagger a_j|0\rangle$ is neglected since it is a sum of terms bilinear in the ξ_s. Indeed, the ground-state expectation value of any operator which has a destruction operator to the right

[28] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957).

and a creation operator to the left, regardless of what is in between, can be neglected according to the above assumption, i.e.,

$$\langle 0|b_\alpha^\dagger\cdots a_i|0\rangle\approx 0.$$

The question of the validity of the assumptions contained in Eq. (20b) for atomic structure cannot be answered with any certainty. Of course it depends strongly on the basis states, and the Hartree-Fock basis would be expected to be most satisfactory. Quantitative work pertinent to this question was done on helium by Green and coworkers who expanded a Hylleras variational wave function into a series of Hartree configurations.[29] The results for that atom showed that the largest ξ_s was ~ 0.03. This then serves as an indication that the assumption may be valid for atomic structure calculations.

With the help of the Fermion commutation rules and the two basic approximations described above, we can now write Eq. (16) as a linear equation for the g's and h's. The entire derivation is tedious, but two examples will be given to illustrate the method. First, consider a very simple case,

$$\langle 0|[A(LM,SM_S,E),C^\dagger(LM,SM_S,\{i\alpha\})]|0\rangle = g(LM,SM_S,E,\{i\alpha\})+\text{terms which contain } \langle 0|a_i^\dagger a_j|0\rangle \text{ or } \langle 0|b_\alpha^\dagger b_\beta|0\rangle.$$

Thus,

$$\langle 0|[A(LM,SM_S,E),C^\dagger(LM,SM_S,\{i\alpha\})]|0\rangle \approx g(LM,SM_S,E,\{i\alpha\}). \quad (21)$$

For the second example, consider one term in V_S

$$V_S'=\tfrac{1}{2}\sum_{i,\alpha,j,\beta}\langle ij|v|\alpha\beta\rangle C(i\alpha)C(j\beta).$$

We now take cognizance of the fact that all the states studied here are singlet states; thus we write

$$C^\dagger(LM,\{i\alpha\})=\sum_{m_\alpha,\mu_\alpha}\frac{(l_\alpha -m_\alpha l_i m_i/LM)}{\sqrt{2}}\delta_{\mu_i\mu_\alpha}C^\dagger(i\alpha), \quad (22)$$

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i.e., the spin designation is dropped from $C^\dagger(LM,SM_S,\{i\alpha\})$. It is understood that these states are eigenstates of total spin with eigenvalue zero.

By straightforward evaluation

$$\langle 0|[A(LM,E),[V_S',C^\dagger(LM,\{k\gamma\})]]|0\rangle$$

$$=\tfrac{1}{2}\sum_{i,\alpha,j,\beta}\langle ij|v|\alpha\beta\rangle\sum_{m_\gamma,\mu_\gamma}(-1)^{m_\gamma}\frac{(l_\gamma -m_\gamma l_k m_k|LM)}{\sqrt{2}}\delta_{\mu_k\mu_\gamma}\langle 0|[A(LM,E),C(i\alpha)(\delta_{kj}\delta_{\gamma\beta}-\delta_{\gamma\beta}a_k^\dagger a_j-\delta_{kj}b_\gamma^\dagger b_\beta)$$

$$+(\delta_{ki}\delta_{\gamma\alpha}-\delta_{\gamma\alpha}a_k^\dagger a_i-\delta_{ki}b_\gamma^\dagger b_\alpha)C(j\beta)]|0\rangle$$

$$=\tfrac{1}{2}\sum_{i,\alpha,j,\beta}\langle ij|v|\alpha\beta\rangle\sum_{m_\gamma,\mu_\gamma}(-1)^{m_\gamma}\frac{(l_\gamma -m_\gamma l_k m_k|LM)}{\sqrt{2}}\delta_{\mu_k\mu_\gamma}\sum_{m_\nu,\mu_\nu}h(L-M,E,\{n\nu\})(-1)^{m_\nu}\frac{(l_\nu -m_\nu l_n m_n|L-M)}{\sqrt{2}}$$

$$\times\delta_{\mu_\nu\mu_n}(-\delta_{ni}\delta_{\nu\alpha}\delta_{kj}\delta_{\gamma\beta}-\delta_{ki}\delta_{\gamma\alpha}\delta_{nj}\delta_{\nu\beta}+\delta_{ik}\delta_{\alpha\nu}\delta_{jn}\delta_{\gamma\beta}+\delta_{kj}\delta_{\gamma\beta}\delta_{ni}\delta_{\alpha\gamma}), \quad (23)$$

where we have used the ground-state approximation and Eq. (19). To simplify the above, a multipole expansion of the Coulomb matrix element is made, and Eq. (23) reduces to

$$\langle 0|[A(LM,E),[V_S',C^\dagger(LM,\{k\gamma\})]]|0\rangle$$

$$=-2\sum_{\{n\nu\}}J_L(\{k\gamma\},\{n\nu\})(-1)^M h(L-M,E,\{n\nu\})+\sum_{m_\gamma,m_\nu,\{n\nu\},L',M'}J_{L'}(\{n\gamma\},\{k\nu\})(-1)^{M'}$$

$$\times(l_\gamma -m_\gamma l_k m_k|LM)(l_\gamma -m_\gamma l_n m_n|L'M')(l_\nu -m_\nu l_k m_k|L'-M')(l_\nu -m_\nu l_n m_n|LM)h(L-M,E,\{n\nu\}), \quad (24)$$

where

$$J_L(\{k\gamma\},\{n\nu\})=(\chi_L(\{k\gamma\},\{n\nu\})[(2l_k+1)(2l_\gamma+1)(2l_n+1)(2l_\nu+1)]^{1/2}(l_\gamma 0 l_k 0|L0)(l_\nu 0 l_n 0|L0))/(2L+1)^2. \quad (25)$$

The symbol $\chi_L(\{k\gamma\},\{n\nu\})$ designates the radial integral in the Lth term of the expansion of the interaction.

Each term in the Hamiltonian is analyzed like V_S' and the following results are found. Referring to Eqs. (6) and (7), the terms K, V_S, and part of W contribute to the eigenvalue equation. The term V_1 describes particle-particle and hole-hole interactions. Since we are working with a model that uses states with only one pair excited, we do not expect this term to contribute; a direct calculation, using the ground-state approximation, shows that it does not. The term V_2 couples one and two pair states. This term does not contribute because of our neglect of the two pair excitations, i.e., using Eq. (19). The contribution from W depends on the central field chosen for the calculation. This will be more fully discussed in Sec. III.

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[29] L. C. Green, M. M. Mulder, C. W. Ufford, E. Slaymaker, E. Krawitz, and R. T. Mertz, Phys. Rev. 85, 65 (1952).

Having indicated the method of derivation, we now write down the eigenvalue equations, both for $C^\dagger(LM,\{i\alpha\})$ and for $C(L-M,\{i\alpha\})$.

$$(\omega_E-\omega_{i\alpha})g(LM,E,\{i\alpha\})-2\sum_{\{j\beta\}}J_L(\{i\alpha\},\{j\beta\})[g(LM,E,\{j\beta\})-(-1)^M h(L-M,E,\{j\beta\})]$$
$$-\sum_{m_\alpha,m_\beta,\{j\beta\},L',M'}J_{L'}(\{j\alpha\},\{i\beta\})(-1)^{M'}(l_\alpha-m_\alpha l_i m_i|LM)(l_\alpha-m_\alpha l_j m_j|L'M')(l_\beta-m_\beta l_i m_i|L'-M')$$
$$\times(l_\beta-m_\beta l_j m_j|L-M)h(L-M,E,\{j\beta\})+\sum_{m_\alpha,m_\beta,\{j\beta\}}\langle\beta i|v|\alpha j\rangle(-1)^{m_\alpha+m_\beta}(l_\alpha-m_\alpha l_i m_i|LM)(l_\beta-m_\beta l_j m_j|LM)$$
$$\times g(LM,E,\{j\beta\})-\sum_{m_\alpha,\{j\}}\gamma_{ij}(l_\alpha-m_\alpha l_i m_i|LM)(l_\alpha-m_\alpha l_j m_j|LM)g(LM,E,\{j\alpha\})$$
$$+\sum_{m_\alpha,m_\beta,\{\beta\}}\gamma_{\alpha\beta}(-1)^{m_\alpha+m_\beta}(l_\alpha-m_\alpha l_i m_i|LM)(l_\beta-m_\beta l_i m_i|LM)g(LM,E,\{i\beta\})=0, \quad (26a)$$

$$(-1)^M(\omega_E+\omega_{i\alpha})h(L-M,E,\{i\alpha\})-2\sum_{\{j\beta\}}J_L(\{i\alpha\},\{j\beta\})[g(LM,E,\{j\beta\})-(-1)^M h(L-M,E,\{j\beta\})]$$
$$+\sum_{m_\alpha,m_\beta,\{j\beta\},L'M'}J_{L'}(\{j\alpha\},\{i\beta\})(-1)^{M'}(l_\alpha-m_\alpha l_j m_j|L'M')(l_\beta-m_\beta l_i m_i|L'-M')(l_\alpha-m_\alpha l_i m_i|L-M)$$
$$\times(l_\beta-m_\beta l_j m_j|LM)g(LM,E,\{j\beta\})-\sum_{m_\alpha,m_\beta,\{j\beta\}}\langle\beta i|v|\alpha j\rangle(-1)^{m_\alpha+m_\beta}(l_\alpha-m_\alpha l_i m_i|L-M)(l_\beta-m_\beta l_j m_j|L-M)$$
$$\times h(L-M,E,\{j\beta\})+\sum_{m_\alpha,\{j\}}\gamma_{ij}(l_\alpha-m_\alpha l_i m_i|L-M)(l_\alpha-m_\alpha l_j m_j|L-M)h(L-M,E,\{j\alpha\})$$
$$-\sum_{m_\alpha,m_\beta,\{\beta\}}\gamma_{\alpha\beta}(-1)^{m_\alpha+m_\beta}(l_\alpha-m_\alpha l_i m_i|L-M)(l_\beta-m_\beta l_i m_i|L-M)h(L-M,E,\{i\beta\})=0. \quad (26b)$$

In the above, the sum over one projection quantum number in a vector coupling coefficient implies a sum over the other. We have introduced

$$\omega_E\equiv E-E_0$$
$$\omega_{i\alpha}\equiv\epsilon_i-\epsilon_\alpha.$$

In Eqs. (26) the first three terms constitute the usual random-phase approximation. The next term is the exchange term which does not contribute to the correlation energy of the high-density electron gas, but there is no reason to neglect it here. The last two terms are self-energy terms, and their contribution depends on the basis set used.

In their present form, the eigenvalue equations are quite general; the principal restriction being the requirement that the ground state of the atom be a closed shell configuration. These equations can be simplified considerably, however, when they are used for the particular atoms studied in this paper. We examine here only correlations among the valence electrons. Thus, the sums over hole states in Eqs. (26) are taken only over the valence shell. Further, this shell contains only s electrons, so there is no sum over the orbital projection quantum number. Since the only excited states considered are ^1P states, all the particle states are p states. The excitation energy is the same for all allowed values of M, so M is chosen equal to zero making all the particle orbital projection quantum numbers also equal to zero. With all the above simplifications Eqs. (26) reduce to

$$(\omega_E-\omega_{i\alpha}+\gamma_{\alpha\alpha})g(10,E,\{i\alpha\})-\sum_{\{j\}}J_1(\{j\alpha\},\{i\alpha\})$$
$$\times[2g(10,E,\{j\alpha\})-h(10,E,\{j\alpha\})]$$
$$+\sum_{\{j\}}(\langle\alpha i|v|\alpha j\rangle-\gamma_{ij})g(10,E,\{j\alpha\})=0, \quad (27a)$$

$$(\omega_E+\omega_{i\alpha}-\gamma_{\alpha\alpha})h(10,E,\{i\alpha\})-\sum_{\{j\}}J_1(\{j\alpha\},\{i\alpha\})$$
$$\times[g(10,E,\{j\alpha\})-2h(10,E,\{j\alpha\})]$$
$$-\sum_{\{j\}}(\langle\alpha i|v|\alpha j\rangle-\gamma_{ij})h(10,E,\{j\alpha\})=0. \quad (27b)$$

The restriction to the valence electrons assumes that the correlation structure for the lower shells is about the same in the ground and singly excited states. It is this assumption which allows the treatment of heavy atoms with the same size matrix as used for light atoms. If, however, the total correlation energy were to be computed instead of the excitation energies, the interactions among all the electrons would have to be treated.

We conclude this subsection by finding the normalization condition on the eigenvectors. We desire

$$\langle LM,E|LM,E'\rangle=\delta_{EE'} \quad (28)$$

for discrete states. This leads to

$$\langle 0|[A(LM,E),A^\dagger(LM,E')]|0\rangle=\delta_{EE'}$$

or

$$\sum_{\{i\alpha\}}[g(LM,E,\{i\alpha\})g(LM,E',\{i\alpha\}) -h(L-M,E,\{i\alpha\})h(L-M,E',\{i\alpha\})]=\delta_{EE'}. \quad (29)$$

For continuum states, the Kronecker delta is replaced by a Dirac delta function.

C. Oscillator Strength and Photoionization Cross Section

The expressions for the oscillator strength and the photoionization cross sections of the transitions considered here both involve the dipole element

$$D=\sum_{M=-1}^{1}|\langle 1M,E|\sum_{s=1}^{N}\mathbf{r}_s|0\rangle|^2. \quad (30)$$

This quantity has spherical symmetry, therefore

$$D=3|\langle 10,E|\sum_{s=1}^{N}z_s|0\rangle|^2. \quad (31)$$

To evaluate Eq. (31) the operator z is expanded in terms of the particle and hole operators

$$z_{o\rho}=\sum_{i\alpha}\langle i|z|\alpha\rangle[C^\dagger(i\alpha)+C(i\alpha)]+\sum_{i,j}\langle i|z|j\rangle a_i^\dagger a_j -\sum_{\alpha,\beta}\langle\alpha|z|\beta\rangle b_\beta^\dagger b_\alpha. \quad (32)$$

Thus

$$D=3|\langle 0|[A(10,E),z_{o\rho}]|0\rangle|^2 =2|\sum_{\{i\alpha\}}\rho\{i\alpha\}[g(10,E,\{i\alpha\})-h(10,E,\{i\alpha\})]|^2, \quad (33)$$

where $\rho\{i\alpha\}$ is the radial integral of r. To arrive at Eq. (33), the same approximations were used as in the derivation of the eigenvalue equations.

The expression for the absorption oscillator strength, averaged over polarizations, is

$$\bar{f}_E=\tfrac{4}{3}\omega_E|\sum_{\{i\alpha\}}\rho\{i\alpha\}[g(10,E,\{i\alpha\})-h(10,E,\{i\alpha\})]|^2, \quad (34)$$

where ω_E is given in atomic units. Similarly, the photoionization cross section is, also in atomic units,

$$\sigma_K=\frac{4\pi^2\omega_E\alpha}{3K}|\sum_{\{i\alpha\}}\rho\{i\alpha\}[g(10,E,\{i\alpha\}) -h(10,E,\{i\alpha\})]|^2. \quad (35)$$

In Eq. (35) α is the fine structure constant, and $K^2/2$ is the kinetic energy of the ejected electron at infinity. The continuum eigenstates are normalized to a delta function in K, i.e.,

$$\langle LM,E|LM,E'\rangle=\delta(K'-K), \quad (36)$$

where E is the energy corresponding to the atomic state with one free electron having a kinetic energy of $K^2/2$. Of course, the summations in Eqs. (34) and Eq. (35) also involve integrations over the continuum.

III. NUMERICAL METHODS

The first step in the numerical evaluation of Eqs. (27) is the selection of a single-particle potential. The Hartree-Fock potential is probably the best choice, but the formidable numerical difficulties associated with generating a complete set of Hartree-Fock orbitals led us to a simpler choice for this first calculation. The potential chosen was the Hartree potential due to $N-1$ electrons for an N electron atom. The charge density of one of the valence electrons was excluded from the potential. This is a physically reasonable potential for the valence orbital as well as all excited orbitals. All the basis states were computed in this potential, however; thus the orbitals belonging to inner shells were computed with too much screening, but these orbitals do not play an essential role in the theory. When Hartree orbitals were not available from the literature, the Thomas-Fermi potential for a positive ion was used.

The effect of this choice of the central potential on the Eqs. (27) will now be accounted for. Consider the last term on the left-hand side of Eq. (27a), $\langle\alpha i|v|\alpha j\rangle -\gamma_{ij}$. When γ_{ij} is written out, this becomes

$$\langle\alpha i|v|\alpha j\rangle-\sum_\gamma{}'\langle j\gamma|v|i\gamma\rangle_{\rm as}-2\langle j\alpha|v|i\alpha\rangle +\langle j\alpha|v|\alpha i\rangle+\langle j|V|i\rangle. \quad (37)$$

The prime on the sum indicates that the valence shell is excluded, and the direct and exchange interaction with the valence shell is written out explicitly. The exchange interaction with the valence shell is exactly the same matrix element that appears as the coefficient of $g(10,E,\{j\alpha\})$ in the second term of Eq. (27a). Thus, those two terms can be combined, leaving from the expression (37)

$$\langle j|V|i\rangle-\sum_\gamma{}'\langle j\gamma|v|i\gamma\rangle_{\rm as}-\langle j\alpha|v|i\alpha\rangle. \quad (38)$$

Because of the definition of V, the above quantity should be small. The deviations of the quantity (38) from zero arise from two causes. First, the potential does not include exchange effects so all the exchange integrals are not accounted for. These exchange integrals involve only shells below the valence shell, however; exchange interactions with the valence shell have been treated exactly. Second, the orbitals γ are not found self-consistently, so the cancellation of their matrix elements with the Hartree potential will not be perfect. Nevertheless, these deviations are assumed small, and only the diagonal terms ($i=j$) of this quantity are retained. The same treatment holds, of course, for Eq. (27b) and the equations to be numerically solved

become

$$(\omega_E-\omega_{i\alpha}')g(10,E,\{i\alpha\})-\sum_{\{j\}}J_1(\{i\alpha\},\{j\alpha\})\times[g(10,E,\{j\alpha\})-h(10,E,\{j\alpha\})]=0, \quad (39a)$$

$$(\omega_E+\omega_{i\alpha}')h(10,E,\{i\alpha\})-\sum_{\{j\}}J_1(\{i\alpha\},\{j\alpha\})\times[g(10,E,\{j\alpha\})-h(10,E,\{j\alpha\})]=0, \quad (39b)$$

where

$$\omega_{i\alpha}'=\omega_{i\alpha}-\gamma_{\alpha\alpha}-\langle i|V|i\rangle+\sum_{\gamma}'\langle i\gamma|v|i\gamma\rangle_{as}+\langle i\alpha|v|i\alpha\rangle. \quad (40)$$

Hartree orbitals from which the potential could be formed were available for beryllium[30] and calcium,[31] while the Thomas-Fermi field was used for magnesium, also calcium, and strontium. The Thomas-Fermi field and the alteration of that field to that of a positive ion was then taken from Gombas.[32] The Schrödinger equation with the above central fields was numerically integrated using a program obtained from J. Babcock of the Rand Corporation. It is a modernization of the program used by Latter[33] in his extensive computations based on the Thomas-Fermi and Thomas-Fermi-Dirac models. The program is described in that paper and will not be further discussed here except to note that it reproduced hydrogen eigenvalues to six significant figures and wave functions to ± 1 in the fifth figure over the entire range of integration. This program produced both the bound and continuum solutions. The asymptotic amplitude of the continuum solutions for delta function normalization is $(2/\pi)^{1/2}$ and the numerical functions were adjusted to this amplitude employing a method described by Bates and Seaton.[34]

For each atom the following orbitals were computed: (1) all the ground-state orbitals, (2) the first five excited, bound, p orbitals (six for beryllium), (3) continuum p orbitals at k intervals of 0.1 from $k=0.1$ to 1.0 for beryllium, $k=0.1$ to 1.2 for magnesium, and $k=0.1$ to 1.6 for the other cases. These k values are in atomic units. The consideration of only these states implies cutoffs in the sums appearing in Eqs. (39). These cutoffs were chosen so they will not affect the data for the first three or four excited states of the atom and the continuum near threshold.

The next step toward the solution of Eqs. (39) is the evaluation of the Coulomb matrix elements using the basis orbitals. We must evaluate Slater F and G integrals to find the $\gamma_{\alpha\alpha}$'s, and also the $\chi_L(\{i\alpha\}),\{j\alpha\})$ must be found which are given by

$$\chi_L(\{i\alpha\},\{j\alpha\})=\int_0^\infty dr_1\int_0^\infty dr_2P_i(r_1)P_j(r_2)\frac{r_<^L}{r_>^{L+1}}P_\alpha(r_1)P_\alpha(r_2),$$

where $P_i(r)$ is the individual orbital for the ith state and

$$r_>=r_2, \quad r_<=r_1 \quad \text{for} \quad r_1<r_2,$$
$$r_>=r_1, \quad r_<=r_2 \quad \text{for} \quad r_1>r_2.$$

These integrals were all found by numerical integration using Simpson's Rule. An indication of the accuracy achieved was obtained by comparing the results from two independent programs. These results were consistent to five figures.

Due to the similarity in form between Eq. (39a) and Eq. (39b) they can be combined by introducing

$$f(10,E,\{i\alpha\})=g(10,E,\{i\alpha\})-h(10,E,\{i\alpha\}). \quad (41)$$

We find

$$(\omega_E{}^2-\omega_{i\alpha}{}'^2)f(10,E,\{i\alpha\})-2\omega_{i\alpha}'\sum_{\{j\}}J_L(\{i\alpha\},\{j\alpha\})\times f(10,E,\{j\alpha\})=0. \quad (42)$$

The sum over states in Eq. (42) includes an integral over the continuum. To solve Eq. (42) for the discrete eigenvalues this integral is replaced by its approximate value using the trapezoidal rule. This reduces the equations to an ordinary linear set which is then solved on the computer.

The above procedure breaks down, however, when solutions corresponding to eigenvalues in the continuum are sought. To see why, we write

$$f(10,E,\{i\alpha\})=\frac{2\omega_{i\alpha}'\sum_{\{j\}}J_L(\{i\alpha\},\{j\alpha\})f(10,E,\{j\alpha\})}{(\omega_E{}^2-\omega_{i\alpha}{}'^2)}. \quad (43)$$

Since $\omega_{i\alpha}'$ and ω_E now have continuous ranges of values, the denominator in Eq. (43) can be zero, and thus $f(10,E,\{i\alpha\})$ has a singularity. From Eqs. (39), however, we see that

$$\frac{g(10,E,\{i\alpha\})}{h(10,E,\{i\alpha\})}=\frac{\omega_E+\omega_{i\alpha}'}{\omega_E-\omega_{i\alpha}'}, \quad (44)$$

and thus the singularity in the eigenvector can be avoided by writing the equations in terms of $h(10,E,\{i\alpha\})$. The Eqs. (39) become

$$h(10,K,\{k\alpha\})=S(\{K\},\{k\})/(\omega_K+\omega_{k\alpha}'), \quad (45)$$

where

$$S(\{K\},\{k\})=2\left[\sum_{\{j\}}^{\{j_0\}}\frac{J_1(\{j\alpha\},\{k\alpha\})\omega_{j\alpha}'h(10,K,\{j\alpha\})}{(\omega_K-\omega_{j\alpha}')}+\int_0^{k_0}\frac{dk'\omega_{k'\alpha}'J_1(\{k\alpha\},\{k'\alpha\})h(10,K,\{k'\alpha\})}{(\omega_K-\omega_{k'\alpha}')}\right], \quad (46)$$

[30] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935).
[31] W. Hartree, D. R. Hartree, and M. F. Manning, Phys. Rev. **59**, 299 (1941).
[32] P. Gombas, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXVI, p. 109.
[33] R. Latter, Phys. Rev. **99**, 510 (1955).
[34] D. R. Bates and M. J. Seaton, Monthly Notices Roy. Astron. Soc. **109**, 698 (1949).

and $\omega_K=I+K^2/2$, where I is the ionization potential. The continuum eigenstate is now designated by K, and the single-particle continuum states are designated by k and k'. The sum over states is explicitly separated into a discrete sum plus an integral, and the cutoffs $\{j_0\}$ and $\{k_0\}$ are introduced. The problem is now reduced to representing the integral in Eq. (46) by a sum of discrete terms. In the region of integration that is not close to the point $\omega_K=\omega_{k'\alpha}'$, the integral is replaced by its approximate value using Simpson's rule. Let us denote the remaining range of k' by 2Δ and write

$$I_0=2\int_{K-\Delta}^{K+\Delta}\frac{dk'\omega_{k'\alpha}'J_1(\{k\alpha\},\{k'\alpha\})h(10,K,\{k'\alpha\})}{(K^2-k'^2)}. \quad (47)$$

This integral is, as yet, not defined as the integrand is singular. Following Rice[35] and Fano[36] we can write

$$I_0=2P\int_{K-\Delta}^{K+\Delta}\frac{dk'\omega_{k'\alpha}'J_1(\{k\alpha\},\{k'\alpha\})h(10,K,\{k'\alpha\})}{(K^2-k'^2)}+\frac{\beta\omega_K J_1(\{K\alpha\},\{k\alpha\})h(10,K,\{K\alpha\})}{K}, \quad (48)$$

where P indicates the principal part and β must be determined as an eigenvalue in the solution of the equations. The treatment of the principal part integral is given in the Appendix, and the final result is that Eqs. (45) are reduced to a discrete linear set.

For the discrete eigenvalues, a matrix diagonalization program written by W. P. Frank of Space Technology Laboratory was used.[37] This program was generally satisfactory; however, if the eigenvalues were closely spaced, occasionally the program would produce incorrect results. This was controlled by scaling, and the incorrect eigenvalues were identified by computing the orthogonality of the resulting eigenvectors.

A matrix inversion program written by B. S. Garbow of Argonne National Laboratory was used for the continuum solutions.[38] The largest matrix studied was 40×40, and the equations were solved to ±2 in the seventh figure in this case. Mesh sizes from $\Delta k=0.1$ to $\Delta k=0.025$ were used. The numerical results for these different meshes varied about 1%, so the results presented are with a mesh of $\Delta k=0.1$.

The evaluation of the dipole moment in Eq. (33) presents problems similar to those encountered in reducing the eigenvalue equations to a discrete set. These problems were handled in just the same manner as were the eigenvalue equations.

IV. NUMERICAL RESULTS

In this section the results of the random-phase approximation applied to beryllium, magnesium, calcium, and strontium are given. The results are given for each atom separately and compared with previous theoretical and experimental work. Some coulomb matrix elements computed for beryllium are displayed in Figs. 1, 2, and 3 to show their general behavior. This behavior was followed by all of the atoms. Also some typical eigenvectors for beryllium are shown in Table I. In what follows, all energies are in atomic units (1 a.u.=27.21 eV), and the photoionization cross sections are listed in megabarns (1 Mb=10^{-18} cm^2).

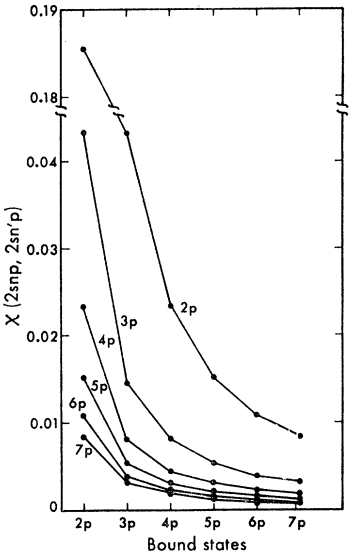

FIG. 1. Beryllium bound-bound matrix elements.

A. Beryllium

We begin with a brief discussion of the coulomb matrix elements. The quantity displayed is the normalized integral with no angular factors, i.e., the $\chi_1(\{i\alpha\},\{j\alpha\})$. In Fig. 1, some bound-bound elements are shown. Note that these elements are largest for the low-lying states and decrease rapidly in the higher states. There are two points to be noted in Fig. 2. First, the continuum states are coupled much more strongly to the lowest bound state than to the higher ones in the important energy range. Second, the bound-free coupling reaches a

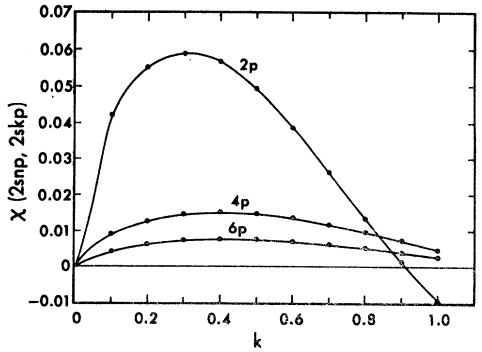

FIG. 2. Beryllium bound-free matrix elements.

[35] O. K. Rice, J. Chem. Phys. **1**, 375 (1933).
[36] U. Fano, Phys. Rev. **124**, 1866 (1961).
[37] SHARE designation F2 RW EIGN and F2 RW VCTR.
[38] SHARE designation F1 AN F402.

TABLE I. Beryllium eigenvectors.

Config.	$^1P(2s-2p)$ $g(10,E,\{i\alpha\})$	$h(10,E,\{i\alpha\})$	$^1P(2s-5p)$ $g(10,E,\{i\alpha\})$	$h(10,E,\{i\alpha\})$
$2s-2p$	0.9963	0.1470	−0.0376	−0.0142
$2s-3p$	−0.1520	0.0246	−0.0415	−0.0036
$2s-4p$	−0.0560	0.0119	−0.0566	−0.0019
$2s-5p$	−0.0303	0.0074	−0.9914	−0.0013
$2s-6p$	−0.0205	0.0052	0.0866	−0.0009
$2s-7p$	−0.0152	0.0040	0.0406	−0.0007
$2s-0.1p$	−0.0683	0.0194	0.0856	−0.0036
$2s-0.2p$	−0.0806	0.0245	0.0743	−0.0047
$2s-0.3p$	−0.0741	0.0248	0.0527	−0.0051
$2s-0.4p$	−0.0587	0.0219	0.0357	−0.0050
$2s-0.5p$	−0.0412	0.0172	0.0238	−0.0046
$2s-0.6p$	−0.0256	0.0118	0.0157	−0.0038
$2s-0.7p$	−0.0132	0.0067	0.0100	−0.0030
$2s-0.8p$	−0.0042	0.0023	0.0062	−0.0022
$2s-0.9p$	0.0019	−0.0011	0.0035	−0.0014
$2s-1.0p$	0.0057	−0.0036	0.0017	−0.0008
	$^1P(2s-0.1p)$		$^1P(2s-0.7p)$	
	$g(10,E,\{i\alpha\})$	$h(10,E,\{i\alpha\})$	$g(10,E,\{i\alpha\})$	$h(10,E,\{i\alpha\})$
$2s-2p$	0.0809	0.0335	0.0247	0.0151
$2s-3p$	0.0715	0.0092	0.0216	0.0081
$2s-4p$	0.0658	0.0050	0.0151	0.0050
$2s-5p$	0.0757	0.0033	0.0114	0.0034
$2s-6p$	0.0757	0.0024	0.0088	0.0026
$2s-7p$	0.0744	0.0018	0.0070	0.0020
$2s-0.1p$	...	0.0094	0.0413	0.0108
$2s-0.2p$	−0.5742	0.0125	0.0624	0.0151
$2s-0.3p$	−0.2458	0.0137	0.0855	0.0179
$2s-0.4p$	−0.1369	0.0137	0.1179	0.0196
$2s-0.5p$	−0.0836	0.0126	0.1758	0.0204
$2s-0.6p$	−0.0529	0.0109	0.3381	0.0201
$2s-0.7p$	−0.0336	0.0088	...	0.0190
$2s-0.8p$	−0.0208	0.0066	−0.2825	0.0172
$2s-0.9p$	−0.0122	0.0046	−0.1222	0.0149
$2s-1.0p$	−0.0064	0.0027	−0.0677	0.0122

maximum a little above the threshold energy. The first point has a significant effect on the photoionization cross section near threshold, as will be explained later. In Fig. 3 some free-free integrals are shown. These integrals vary smoothly and generally have maximums near their diagonal values. The maximum values themselves climb to a maximum (in Fig. 3, this occurs near $k=0.8$) and then decrease slowly.

Typical beryllium eigenvectors are shown in Table I. The amount of mixing of the configurations is quite small. However, the ground-state correlations, i.e., the h amplitudes play an important role in the numerical results. These correlations are much stronger in the $(2s-2p)$ configuration than in the higher ones.

TABLE II. Excitation energies of beryllium above the ground state.

Level	E_B a.u.	E_C a.u.	E_{rpa} a.u.	E_L a.u.	E_{obs} a.u.
$^1P(2s-2p)$	0.107	0.202	0.188	0.149[a]	0.194
$^1P(2s-3p)$	0.219	0.266	0.266		0.274
$^1P(2s-4p)$	0.251	0.292	0.292		0.306
$^1P(2s-5p)$	0.265	0.311	0.311		
Ionization limit		0.333			0.343

[a] Reference 39.

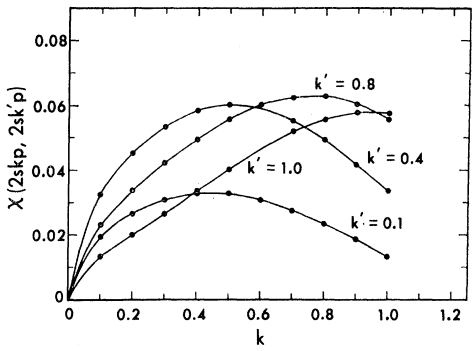

FIG. 3. Beryllium free-free matrix elements.

Excitation energies are listed in Table II. The notation is as follows: E_B—the difference between the particle energy and the hole energy, i.e., $\epsilon_i-\epsilon_\alpha$. This is the excitation energy in the central field with no corrections. E_C—the excitation energy computed in first-order perturbation theory. E_{rpa} the excitation energy computed in the random-phase approximation. E_L—excitation energies found by previous theoretical calculations, and E_{obs}—the experimental energies.

From Table II, it is seen that the energies are represented well by first-order perturbation theory, and, other than a 5% shift in the lowest energy, the random-phase approximation correlations have a negligible effect. The value of E_L was computed by solving the Hartree-Fock equations for the $^1S(2s-2s)$ ground state and the $^1P(2s-2p)$ excited state and subtracting the energies.[39]

Beryllium oscillator strengths are listed in Table III.

TABLE III. Oscillator strengths of beryllium from the ground state.

Level	f_C	f_{rpa}	f_L
$^1P(2s-2p)$	2.34	1.71	1.82[a]
$^1P(2s-3p)$	0.0280	0.0030	
$^1P(2s-4p)$	0.0148	0.0007	
$^1P(2s-5p)$	0.0079	0.0012	

[a] *Landolt-Börnstein Tables*, edited by K. H. Hellwege (Springer-Verlag, Berlin, 1950), Vol. 1, Part 1, p. 264.

The notation is the same as in Table II; f_C is computed with E_C and the bare dipole moment.[39a] In this atom as well as the others that are studied, the lowest energy transition, the "resonance" transition, has a dipole moment much larger than the others. This means that, due to the coupling, the dipole moments of the higher transitions in the random-phase approximation are affected strongly by the resonance transition. So strongly in fact that very weak coupling with the

[39] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A154**, 588 (1936).

[39a] *Note added in proof*. The phrase "bare dipole moment" used in this section means the dipole moment computed in the central-field model.

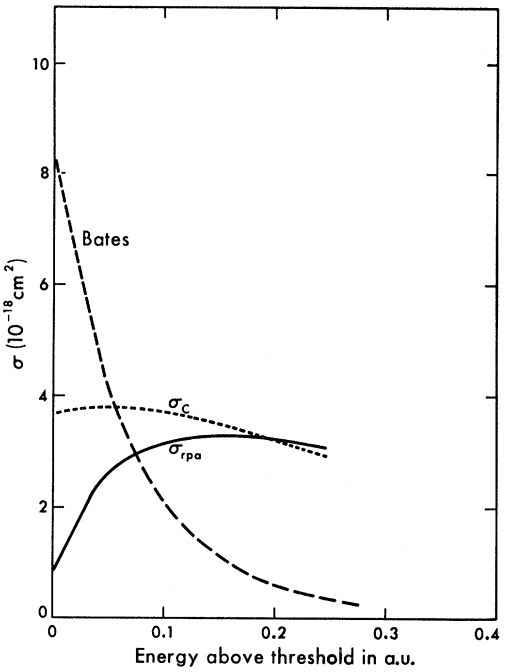

FIG. 4. Photoionization cross section of beryllium.

resonance transition produces a change in the dipole moment of an order of magnitude or more. This circumstance indicates that the oscillator strengths to the higher levels are very difficult to calculate with any hope of accuracy, and probably a model more refined than the random-phase approximation is necessary. Certainly, a central-field approximation is not adequate for this purpose. Another difficulty in the present calculation is that the eigenvalues of the higher levels differ only in the 4th figure from the diagonal matrix elements so that the corresponding eigenvectors will not be accurate.

In Table III, it is seen that the f_{rpa}'s for the higher levels are much smaller than the f_C's. This arises because the dipole moment of the resonance level has the opposite sign from the other dipole moments, so a cancellation occurs. The resonance oscillator strength is reduced principally because of the ground-state correlations. The vector that is important in computing dipole moments is $f(10,E,\{i\alpha\})$, as can be seen from Eq. (33). When $h(10,E,\{i\alpha\})$ is sizable, i.e., when ground-state correlations are important, $f(10,E,\{i\alpha\})$ is quite a bit smaller than $g(10,E,\{i\alpha\})$, and since the dipole moment is squared, this size effect is doubled. The value of f_L was computed with the Hartree-Fock wave functions of Ref. 39, and the experimental energy. There is, at present, no experimental data available for these oscillator strengths. Figure 4 shows the photoionization cross sections for low energy. The decrease of σ_{rpa} compared to σ_C is due to cancellation with the resonance dipole moment as explained above. As higher energies are reached, this effect diminishes, and σ_{rpa} and σ_C approach each other. Even at high energies, however, the ground-state correlations have an effect so the two values need not agree. There is no experimental information, but σ_{rpa} and σ_C are plotted along with a calculation by Bates[40] who uses a coulomb wave function for the continuum states and an analytic function, fitted to a Hartree function, for the bound state. Figure 4 amply demonstrates that the cross section is sensitive to the wave functions used.

B. Magnesium

No Hartree field was available for magnesium, so the Thomas-Fermi positive ion field was used. The excitation energies are listed in Table IV. The results

TABLE IV. Excitation energies of magnesium above the ground state.

Level	E_B a.u.	E_C a.u.	E_{rpa} a.u.	E_L a.u.	E_{obs} a.u.
$^1P(3s-3p)$	0.109	0.161	0.151	0.166[a]	0.160
$^1P(3s-4p)$	0.179	0.213	0.213		0.225
$^1P(3s-5p)$	0.203	0.238	0.238		0.249
Ionization Limit		0.269			0.281

[a] Reference 13.

are very similar to the beryllium results. The value of E_L was calculated by Trefftz, who used a configuration interaction method using Hartree-Fock basis functions.[13]

The oscillator strengths in Table V to the levels of magnesium above the resonance level show the opposite behavior to those of beryllium. They are enhanced relative to the f_C's because, in this case, the resonance dipole moment has the same sign as the others. The value of f_L was computed by Trefftz using the wave functions mentioned above.[13]

The photoionization cross sections are plotted in Fig. 5. The coupling to the resonance level is responsible for the high value at threshold. The dipole moment changes sign resulting in a minimum in the cross-section curve. The experimental work by Ditchburn and Marr[41] was not carried out far enough to observe this minimum, but it probably exists because such a minimum is

TABLE V. Oscillator strengths of magnesium from the ground state.

Level	f_C	f_{rpa}	f_L	f_{obs}
$^1P(3s-3p)$	2.77	1.85	1.674[a]	1.2±0.3[b]
$^1P(3s-4p)$	0.0524	0.184		
$^1P(3s-5p)$	0.0099	0.0466		

[a] Reference 13.
[b] Reference 9.

[40] D. R. Bates, Monthly Notices Roy. Astron. Soc. **106**, 423 (1956).
[41] R. W. Ditchburn and G. V. Marr, Proc. Phys. Soc. (London) **A66**, 655 (1953).

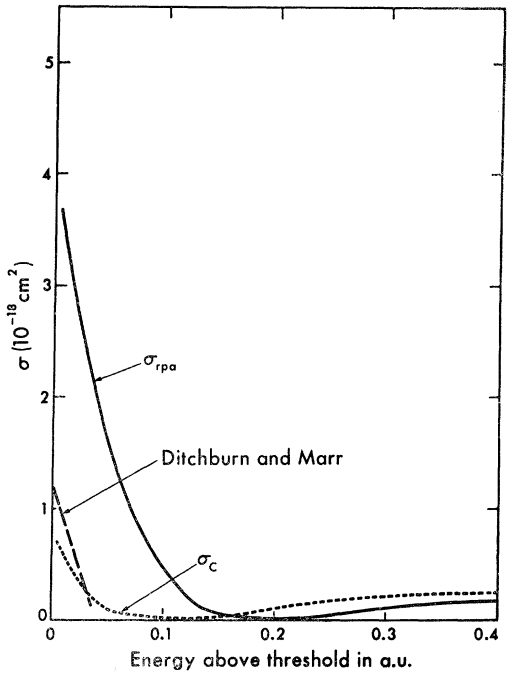

FIG. 5. Photoionization cross section of magnesium.

observed for calcium, and its theoretical explanation is the same as here.

C. Calcium

The Hartree and Thomas-Fermi basis were both used for calcium in order that a comparison could be made. The energy values are comparable in the two cases, but differences in the oscillator strengths and photo-ionization cross section occur. Calcium, unlike beryllium and magnesium, has doubly excited configurations ($3d$-np) that are comparable in energy to the configurations studied here. As mentioned earlier, these configurations are not included in the theory, and this shortcoming is apparent in the numerical results.

The excitation energies are listed in Table VI. The

TABLE VI. Excitation energies of calcium from the ground state.

Level	$E_B^{T.F.}$ a.u.	$E_C^{T.F.}$ a.u.	$E_{rpa}^{T.F.}$ a.u.	E_B^{H} a.u.	E_C^{H} a.u.	E_{rpa}^{H} a.u.	E_L a.u.	E_{obs} a.u.
$^1P(4s-4p)$	0.054	0.127	0.121	0.071	0.129	0.122	0.1045[a] 0.1153[b]	0.108
$^1P(4s-5p)$	0.102	0.180	0.180	0.129	0.185	0.185		0.190
$^1P(4s-6p)$	0.121	0.203	0.203	0.149	0.207	0.207		0.200
Ionization limit		0.234						0.225

[a] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A164**, 167 (1938).
[b] Reference 14.

first-order perturbation theory values are not as accurate as in the previous two cases. The value of $E_L=0.1045$ was obtained by a Hartree-Fock calculation; the value of $E_L=0.1153$ was calculated by Trefftz who used five Hartree-Fock configurations plus a polarization potential.[14]

TABLE VII. Oscillator strengths of calcium from the ground state.

Level	$f_C^{T.F.}$	$f_{rpa}^{T.F.}$	f_C	f_{rpa}^{H}	f_L	f_{obs}
$^1P(4s-4p)$	5.19	3.80	4.02	2.82	2.27[a] 1.46[b]	1.49[c]
$^1P(4s-5p)$	0.062	0.221	0.048	0.168		0.0374[c]
$^1P(4s-6p)$	0.010	0.052	0.008	0.043		0.0602[c]

[a] Table III, Ref. a.
[b] Reference 14.
[c] Reference 10, 11.

The listing of the oscillator strengths in Table VII shows a substantial difference between the Hartree and the Thomas-Fermi models. The bare dipole matrix element calculated with the Thomas-Fermi wave functions is about 15% larger than the Hartree value. The value of $f_L=2.27$ was computed with Hartree-Fock functions, while the other f_L value was obtained by Trefftz in the same calculations that gave the excitation energy mentioned above. Trefftz took the geometric mean of the dipole length element and the dipole velocity element to arrive at the listed number. The experimental f values were obtained by Russian workers quite recently, and the accuracy is stated at a few percent. The fact that the second level has a smaller f than the third has also been observed by other workers. This behavior is not present in f_C or f_{rpa} because it is caused by mixing with the $^1P(3d-4p)$ level.

The photoionization cross section close to threshold has been measured by Ditchburn,[42] and he finds that the $(3d-np)$ ^1P and ^3P series limit lies above threshold, so the autoionization lines from this series are very strong. He attempts to subtract out these lines to find the absorption arising from the $(4s-kp)$ continuum, but it seems that a theoretical calculation of the cross section must take the $(3d-np)$ series into account. As was stated above, the random-phase approximation does not account for this series, so we do not expect satisfactory results for the cross section.

The photoionization cross sections for calcium are plotted in Fig. 6 along with the experimental data. The fact that σ_C^H agrees with experiment at threshold is, in our opinion, just a coincidence. The enhancement of σ_{rpa}^H is due to coupling with the resonance level, as in magnesium. A previous theoretical calculation by Bates and Massey, using Hartree-Fock wave functions, gives a threshold value of $\sigma\approx 23$ Mb.[17]

D. Strontium

The calculational results resemble those for calcium. The problem of the doubly excited configurations is present here as the $4d$ shell lies just above the $5s$ shell. The Thomas-Fermi basis is used. The excitation energies are given in Table VIII.

[42] R. W. Ditchburn, Proc. Roy. Soc. (London) **A256**, 53 (1960).

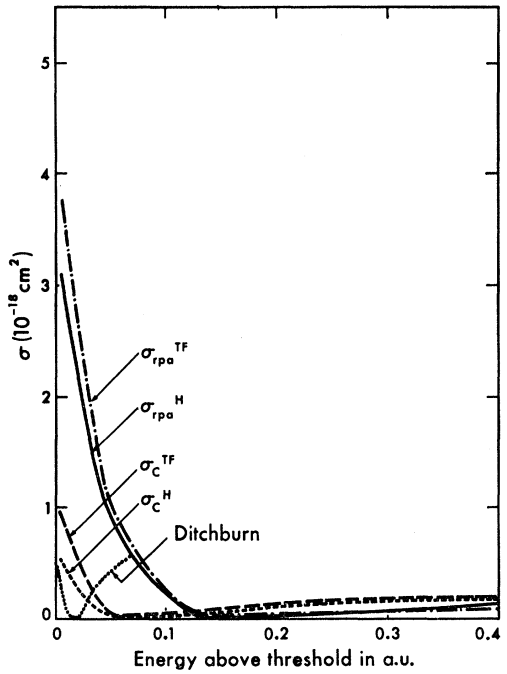

FIG. 6. Photoionization cross section of calcium.

The oscillator strengths are given in Table IX. The experimental values are from the same group that measured the calcium lines. Again the second level has a smaller f than the third, and the explanation is the same as for calcium. The value of f_L was calculated from the Bates-Damgard tables which are based on the Coulomb approximation.

TABLE VIII. Excitation energies of strontium above the ground state.

Level	E_B a.u.	E_C a.u.	E_{rpa} a.u.	E_{obs} a.u.
$^1P(5s-5p)$	0.054	0.112	0.106	0.099
$^1P(5s-6p)$	0.103	0.154	0.154	0.155
$^1P(5s-7p)$	0.121	0.174	0.174	0.177
Ionization limit		0.202		0.209

Recent measurements of the photoionization cross section by Hudson and Young indicate that the $(4d-np)$ series does not strongly affect the $(5s-np)$ continuum near threshold, in contrast to calcium.[16] Thus, the value of σ_{rpa} may have more meaning in this case, and indeed it is the right order of magnitude at threshold as can be seen in Fig. 7.

TABLE IX. Oscillator strengths of strontium from the ground state.

Level	f_C	f_{rpa}	f_L	f_{obs}
$^1P(5s-5p)$	4.60	3.18	1.80[a]	1.54[b]
$^1P(5s-6p)$	0.057	0.228		0.0052[b]
$^1P(5s-7p)$	0.010	0.057		0.0110[b]

[a] C. W. Allen, *Astrophysical Quantities* (The Althone Press, London, 1955), Chap. 4, p. 77.
[b] Reference 12.

V. DISCUSSION

As was stated earlier, the main purpose of this study was to examine the qualitative effects of electron correlations on the calculation of atomic properties, and not to seek close agreement with experimental data at the present time. We see from the results that the correlations have a small effect on the excitation energies; the largest shift is about 5% for the lowest energy, and there is no appreciable shift in the higher energies. The resonance oscillator strengths are lowered about 30% from their bare values, while the oscillator strengths to higher levels and the photoionization cross sections near threshold are changed by orders of magnitude.

The question arises as to why the correlated values of the resonance oscillator strengths are not closer to observed values, and, in our opinion, the answer is in the basis states used. If a Hartree-Fock basis had been used, the criteria for the ground-state approximation in Sec. II would have been more nearly met, and we could expect more accurate results. For example, a shift in the resonance oscillator strength of calcium of about 30% is needed to lower the f value from 2.27 (see Table VIII) to about 1.60 (close to the observed value). Of

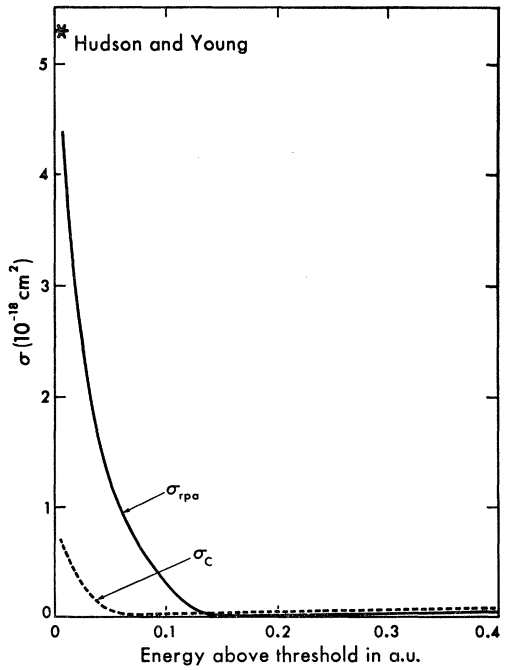

FIG. 7. Photoionization cross section of strontium. The asterisk marks the recent experimental value of Hudson and Young (Ref. 16).

course, it may be that some other kinds of correlations must also be included in any quantitative theory.

The situation is less clear for the higher oscillator strengths and photoionization cross sections. Their calculation seems to be very difficult because of the large change in their value that weak coupling with the resonance level gives. An additional difficulty arises when there are doubly excited configurations of comparable energy present (autoionization in the continuum). In this case, the random-phase approximation is just not adequate. In general, a more refined model than is used here will be necessary for accurate calculation of these quantities.

In the application of the random-phase approximation to the infinite electron gas and to nuclei, collective states are found, i.e., states that are superpositions of many single-particle excitations with each excitation having about equal weight. These states have energies lying above the single-particle excitations and, in nuclei, can have greatly increased dipole moments.

Little indication of such collective states was found in the present calculation, and this can be understood by comparing these other theories with the present atomic calculation. In nuclei, for example, the unperturbed spectrum treated consists of a group of single-particle excitations, all of about the same energy and the same symmetry. The interaction matrix element used is typically 20 to 30% of the excitation energies. Since these states are so closely spaced and the interaction is so large, strong mixing can occur and collective states arise. On the other hand, the excitation spectrum of an atom is not bunched at certain energies, but is spread over the entire energy range. Also the interaction matrix elements approach 20 to 30% only in the lowest excited states; in the higher states, they are much weaker. Thus, the occurrence of a collective state in an atom is, *a priori*, much less likely, and the detailed calculations presented here bear this out. Of course the nuclear structure calculations have never been carried out with realistic wave functions but, instead, with oscillator wave functions. The collective effects in nuclei are also greatly enhanced by interference effects in the dipole-matrix element of the kind found here for atoms. It may well turn out that more realistic treatments of the nuclear photoeffect will lead to a physical picture closer to the one found here than to the degenerate infinite Fermi gas. In any case, it does not seem appropriate to describe the correlated atomic states calculated here as collective in the simple classical meaning of the word.

APPENDIX

The problem is to represent the principal part integral in Eq. (48) as a sum of terms involving $h(10,K,\{k'\alpha\})$ at the mesh points $K-\Delta$, K, $K+\Delta$. This is accomplished by writing $h(10,K,\{k'\alpha\})$ and $J_1(\{k\alpha\},\{k'\alpha\})$ in the interval $K-\Delta$ to $K+\Delta$ by three point Lagrange interpolation, i.e., let

$$K_1=K-\Delta,$$
$$K_2=K,$$
$$K_3=K+\Delta,$$

then

$$h(10,K,\{k'\alpha\}) = \frac{(k'-K_1)(k'-K_2)h(10,K,\{K_3\alpha\})}{2\Delta^2} - \frac{(k'-K_1)(k'-K_3)h(10,K,\{K_2\alpha\})}{\Delta^2} + \frac{(k'-K_2)(k'-K_3)h(10,K,\{K_1\alpha\})}{2\Delta^2} \quad \text{(A1)}$$

with a similar expression for $J_1(\{k\alpha\},\{k'\alpha\})$. When these expressions are substituted back into the integral, the result is

$$P\int_{K-\Delta}^{K+\Delta} \frac{dk'\omega_{k'\alpha}'J_1(\{k\alpha\},\{k'\alpha\})h(10,K,\{k'\alpha\})}{(K^2-k'^2)} = G_1(k,K,\Delta)h(10,K,\{K_1\alpha\})+G_2(k,K,\Delta) \times h(10,K,\{K_2\alpha\})+G_3(k,K,\Delta)h(10,K,\{K_3\alpha\}), \quad \text{(A2)}$$

where the G's are rather complicated coefficients involving integrals of the form

$$P\int_{K-\Delta}^{K+\Delta} \frac{dkk^N}{(K^2-k^2)} \quad \text{(A3)}$$

and values of $J_1(\{k\alpha\},\{k'\alpha\})$ at the mesh points. Since these are known quantities, the G coefficients can be evaluated, and the representation in Eq. (A2) is now suitable for numerical treatment.